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Inhibition of Microbiologically Influenced Corrosion

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Two polydimethylsiloxane (PEG) coatings have produced dramatic increases in the abiotic corrosion resistance of 4340 steel in 0.6M NaC1 solutions. The coatings were selected based on the mechanical sensing model of microbial attachment and were designed to suppress attachment as well as prevent corrosion. Exposure of the PEGS to marine microorganisms and the estuary waters showed that the degree of colonization by organisms was less on the silicone surfaces than on the untreated metal or rigid surfaces as would be predicted by the mechanical sensing model. A second approach to understanding colonization and determining effective inhibitors considers the metal to play an active role in attracting microorganisms through the release of metal ions (corrosion), local pH changes (corrosion), or by its surface charge character. Preliminary results indicate that a relationship between corrosion, the nutrient quality of the substrate for microorganisms, and microbial colonization may exist.

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I. INTRODUCTION

Bacteria and other microorganisms attach and colonize the surface of metals that are exposed to aquatic environments and form biofilms (1-9). The physical presence and metabolic processes of the microorganisms in the biofilm produce chemical changes at the biofilm/metal interface. These changes, in turn, alter the electrochemical characteristics of the metal and thereby influence its corrosion behavior. This process is referred to as microbiologically influenced corrosion, MIC. Biofilm formation resulting in MIC has been recognized by the engineering community as a significant factor in reducing the useful lifetime of equipment (2-9). Experience has shown that MIC becomes important when microbial colonization of immersed metal surfaces becomes significant, and high corrosive activity is correlated with the spatial organization of the mixed microbial population into consortia, with the activities of the various organisms being synergistic.

It is well known that microorganisms can change their surface characteristics in response to changes in the environment (10-13). For example, it has been demonstrated that physiological differences exist between the sessile and planktonic cells of the same bacterium (10, 12,13). The characteristic that is emphasized here is the exceptional ability of microorganisms to change phenotypic expression as a result of environmental stimuli. The exact nature of the stimulus/stimuli that trigger phenotypic changes in microorganisms allowing them to become irreversibly adsorbed onto metal surfaces is not totally clear and could be chemical and/or physical in nature. The goals of this work are: (1) to identify the nature of the stimuli that induce microbial colonization of metallic surfaces; and (2) to identify inhibitors and/or coatings that would prevent, inhibit, or disrupt microbial colonization of the surface leading to the formation of the mixed microbial communities, and thereby, inhibit MIC.

II. Dimethylsilcones and the Mechanical Sensing Model

A. Background

Microbes do not colonize all surfaces equally, but exhibit preferences among immersed materials. There are two classes of materials which seem to be much more effective than others in resisting colonization: the dimethylsilicones (DMS) and the polyethylene oxide (PEO) linear polymers. The monomeric units of which these polymers are composed are quite different in their properties. DMS is a hydrophobic material with exposed methyl groups, while the PEO chain is a hydrophilic material due to the exposed ether oxygen atoms present in every monomeric unit, and which are hydrogen bonding sites available for interaction with water. The difference implies that if there is a common mode for preventing attachment by these materials, it must lie in the properties of the polymer as a whole. There is a group of properties of these polymers which is shared: it is their chain mobility and consequent high configurational entropy, and low resistance to deformation of the polymer chains at the material surface.

Belas, Simon, and Silverman (14) have shown that certain marine vibrio bacteria, which can be cultured in both a liquid medium and on a solid gel surface, change their form depending on their situation. This change is quite dramatic, because their liquid medium forms only have flagellae at one end, with which they swim, whereas the solid medium forms grow lateral flagellae, which grow out from a large number of sites along the lateral surface of the cells. The change between these forms is controlled by the activation of a particular set of genes when the organism senses that it is on or close to a surface. The only stimulus which has been found to induce this change, (other than the presence of a surface) is a great increase in the viscosity of the medium. It thus appears that a mechanical sensing mechanism is involved. There are many mechanical sensory cells known to biology, and they seem to operate in the same way. That is, a deformation of the cell membrane causes a change in the ionic currents across it, which

are controlled by membrane pore structures. Thus, the control of membrane fluxes is disturbed by membrane mechanical deformation. In addition to this mechanism having been found in sensory cells whose function is to sense mechanical stimuli, recent reports indicate that this phenomenon is more general. Cells which normally function in a coherent tissue require a surface to grow on if they are to function properly. These cells are called "anchorage dependent". Their functioning seems to depend upon their approaching a surface suitable for them, upon which they lose their rounded liquid-medium form, and spread out to a much flatter form which results in an increased number of attachment points to the immersed surface. Surfaces upon which strong attachment points do not seem to form do not lead to the change in cell shape which is correlated with their normal functioning. Leonid Margolis and co-workers (15-17) have recently reported that the attachment of animal tissue cells to such surfaces causes a change in the ratio of cellular ionic fluxes, so that the internal pH of cells changes when they accomplish proper attachment. Thus, a signal dependent on the stressing of the cell membrane, thereby affecting membrane ion flux, appears to be required for the transformation of anchorage-dependent cells into their characteristic form for normal function on a surface or in a tissue. A surface which has very little tendency to induce such changes in cells is polydimethylsiloxane.

B. Materials and Methods

Two candidate silicone compounds, PEG-015 and PEG-060, were selected based on the mechanical sensing mechanism of microbial attachment. PEG-015 and PEG-060 are polydimethylsiloxane polymers with the 15 and 60 designations referring to chain length before polymerization. Films of varying rigidity were prepared from commercially available components purchased from Huls Inc. (now United Technologies). The two liquid components are a prepolymer and a catalyst. Films were prepared by mixing the two liquid components in varying ratios (by weight).

Type 4340 steel coupons (1/2 inch square) or 1/2 inch rod type samples that were 1 inch in diameter were polished to a 600 grit finish. The samples were then coated with either the PEG-015 or PEG-060 using a mold technique. The coupons were coated by placing them on a pad of silicone polymer cured at a 5:1 prepolymer:catalyst ratio, and then covered with silicone films in which the ratios of prepolymer:catalyst was varied. In the case of the rod type samples, a mold was made and placed around the polished face. The PEG compounds were then poured into the mold and allowed to dry. The thickness of the coatings for the coupons and the rod type samples ranged from 230 to 850 μm. The film thickness was measured by light section microscopy, making a refractive index correction by comparison with a sample of a silicone film cast upon a microscope slide made thick enough to be measured with a micrometer.

The silicon coated and untreated rod type samples were examined in abiotic electrochemical tests; while the coated and untreated coupons were exposed to the CG-59 mixed community of marine microorganisms which contains sulfate-reducing bacteria. The CG-59 mixed community was originally isolated from corroding seawater piping aboard the USS Princeton and has been shown to cause MIC on a variety of materials including copper, copper-nickel alloys, mild steels, and Monel 400 (18,19). This mixed community of marine microorganisms was cultured and is maintained at NSWC White Oak.

Silicon coated 4340 steel samples were also prepared by dip coating. Rectangular (3/4" by 2") coupons (600 grit surface finish) were suspended in the liquid resin and withdrawn vertically using an electric motor at a rate of 1 mm per minute. The coupons were hung to cure in an air-conditioned room at 25° until the residual liquid in the mixing cup became rigid, usually 24 hours. The coating thicknesses ranged from 22 to 60 μm. In initial tests, corrosion occurred at the edges of the dipped sample due to thinning of the coatings at the sharp edges. Samples were then, after dipping and curing, held in contact with a small amount of additional liquid resin in a trough to cover the edges, and these additional portions of polymer were allowed to cure. This

process provided a very thick (1-2 mm) covering of polymer at the edges of the samples. These samples were examined in abiotic electrochemical tests. The silicones were also immersed in the estuary at the Smithsonian Laboratory in Edgewater, Maryland for six weeks.

Abiotic, electrochemical measurements were made in either deaerated or quiescent 0.6M NaCl solution using a conventional corrosion cell. The samples were immersed in the solution for 24 hours prior to polarization to establish a steady state open circuit potential. Anodic and cathodic polarization curves for treated and untreated 4340 steel samples were then determined potentiostatically by stepping the potential in 25 or 50 mV increments from the corrosion potential in the anodic or cathodic direction and allowing the current to reach a steady state value. Usually 15 to 20 minutes were required at each potential. The polarization curves were used to determine if there were any defects in the coating. The *ac* impedance measurements were made during a 10 day period in quiescent 0.6M NaCl solution using a conventional corrosion cell. Potentials are reported relative to the saturated calomel electrode (sce).

C. Results and Discussion

Abiotic Electrochemical Measurements

In initial tests with the dip coated samples, as discussed above, corrosion occurred at the edges of the these sample due to thinning of the coatings and bare areas at the sharp edges. These defects were readily detected when the samples were immersed in the chloride solution and polarized anodically, i.e. the currents densities increased as potential was increased (made more positive). See for example the curve in Figure 1 labeled "PEG Coated Steel Defect in Coating". Also, corrosion was visibly evident at the edges of the sample. These results are important in that they show that the polarization technique could be used to quickly determine the presence of pores or defects.

Figure 1 also shows anodic polarization curves for two 4340 steel samples and two PEG coated steel samples without defects. The anodic polarization curves show that the current density of the untreated 4340 steel samples increased as the potential was increased (made more positive) indicating general corrosion. However, the current densities on 4340 samples with defect free PEG-015 coatings (produced by dipping) remained very low, less than 0.6 nA/cm^2. Subsequent, examination of the defect free silicone coated 4340 steel surfaces using optical and scanning electron microscopy showed no sign of general or localized corrosion. In contrast, the untreated 4340 steel experienced uniform corrosion with some sites of pitting. Visible corrosion was noted on untreated 4340 samples after less than 1 hour of exposure to the chloride solution. Corrosion rates for untreated 4340 steel and nominal corrosion rates for defect free PEG coated steels are listed in Table 1. The measured current values for the PEG coated samples were at the lower detection limit of the potentiostat so that calculated current densities and corrosion rates presented in Table 1 are nominal values. The important point is that defect free PEG coatings were produced in thicknesses of engineering significance and these coatings provided an effective barrier layer that prevented the underlying metal from corroding.

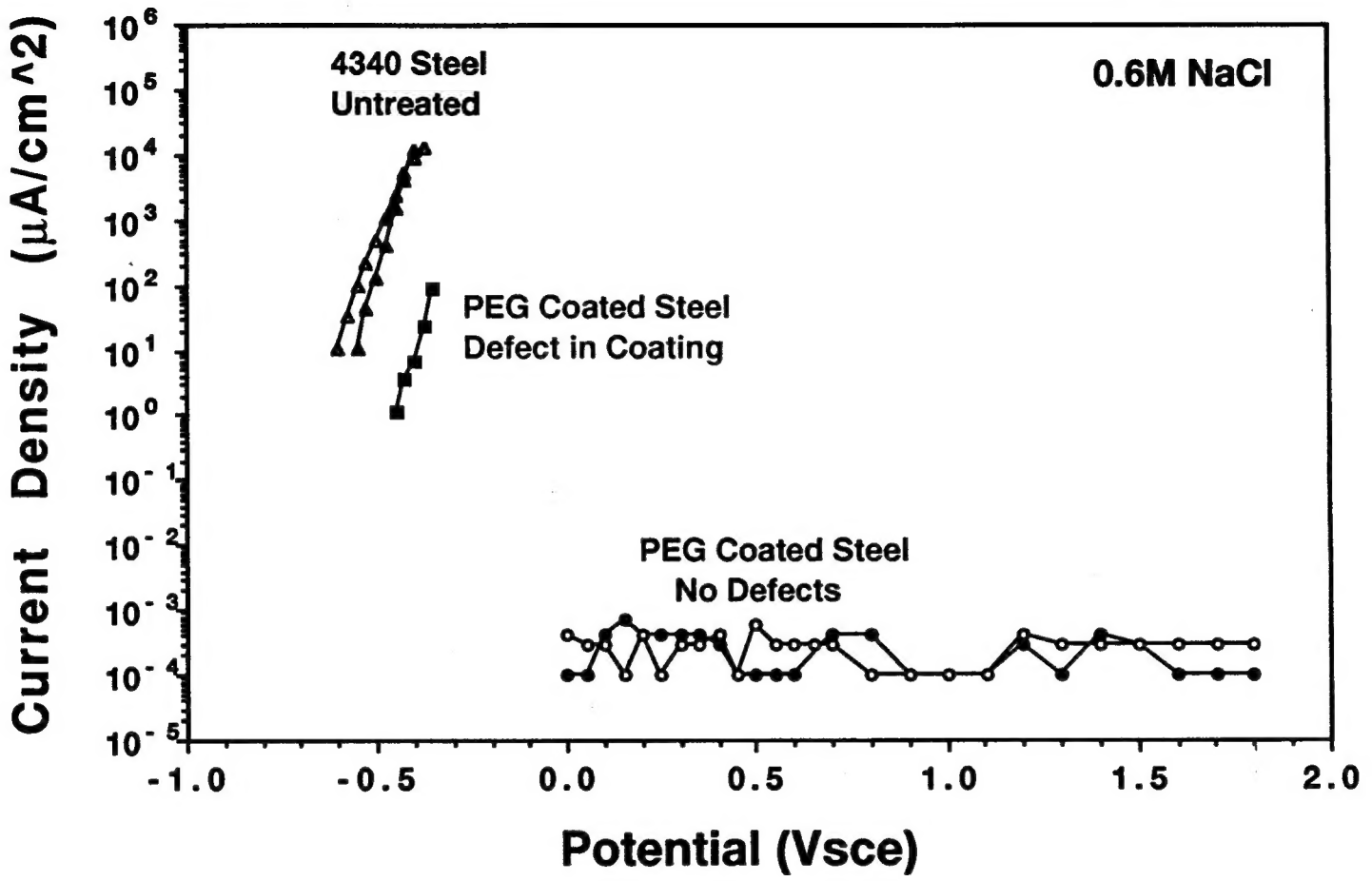

Figure 1. Anodic polarization curves for two 4340 steel samples, a PEG coated steel sample with a defect(s) in the coating, and two PEG coated steel samples without defects.

Table 1. Abiotic corrosion behavior of 4340 steel with and without silicone treatments exposed to quiescent, 0.6 M NaCl solutions.

Treatment	Exposure (Days)	Coating Thickness (μm)	Corrosion Current Density ($\mu A/cm^2$)	Corrosion Rate (mils/year)
None	1	-	9	4.8
PEG-060	1	860	1×10^{-3}*	4.6×10^{-4}
PEG-060	10	250	1×10^{-3}*	4.6×10^{-4}
PEG-015	1	230	1×10^{-3}*	4.6×10^{-4}
PEG-015	1	47	1×10^{-4}*	4.6×10^{-5}
PEG-015	1	22	1×10^{-4}*	4.6×10^{-5}

*Nominal values - the measured current values are at the lower detection limit of the potentiostat.

Figure 2 shows polarization resistance values obtained from 4340 steel and 4340 steel coated with PEG-060 immersed in quiescent, 0.6M NaCl solutions for 10 days. These values were determined using *ac* impedance. The impedance results and visual examinations show that the 4340 steel undergoes corrosion shortly after immersion. The polarization resistance values for the silicone coated 4340 steel remain high, 10^8 ohm/cm^2, for the 10 day period indicating that the PEG was a good barrier coating, i.e. there were no pinholes in the coating and the protective nature of the PEG did not degrade during the exposure. A decreasing value of polarization resistance would indicate that ions or water have penetrated the coating or that ions were being transported through the film, and that charge transfer reactions were occurring at the coating/metal interface. In general, a polarization resistance value of 10^6 ohm-cm^2 or below indicates a non-protective coating.

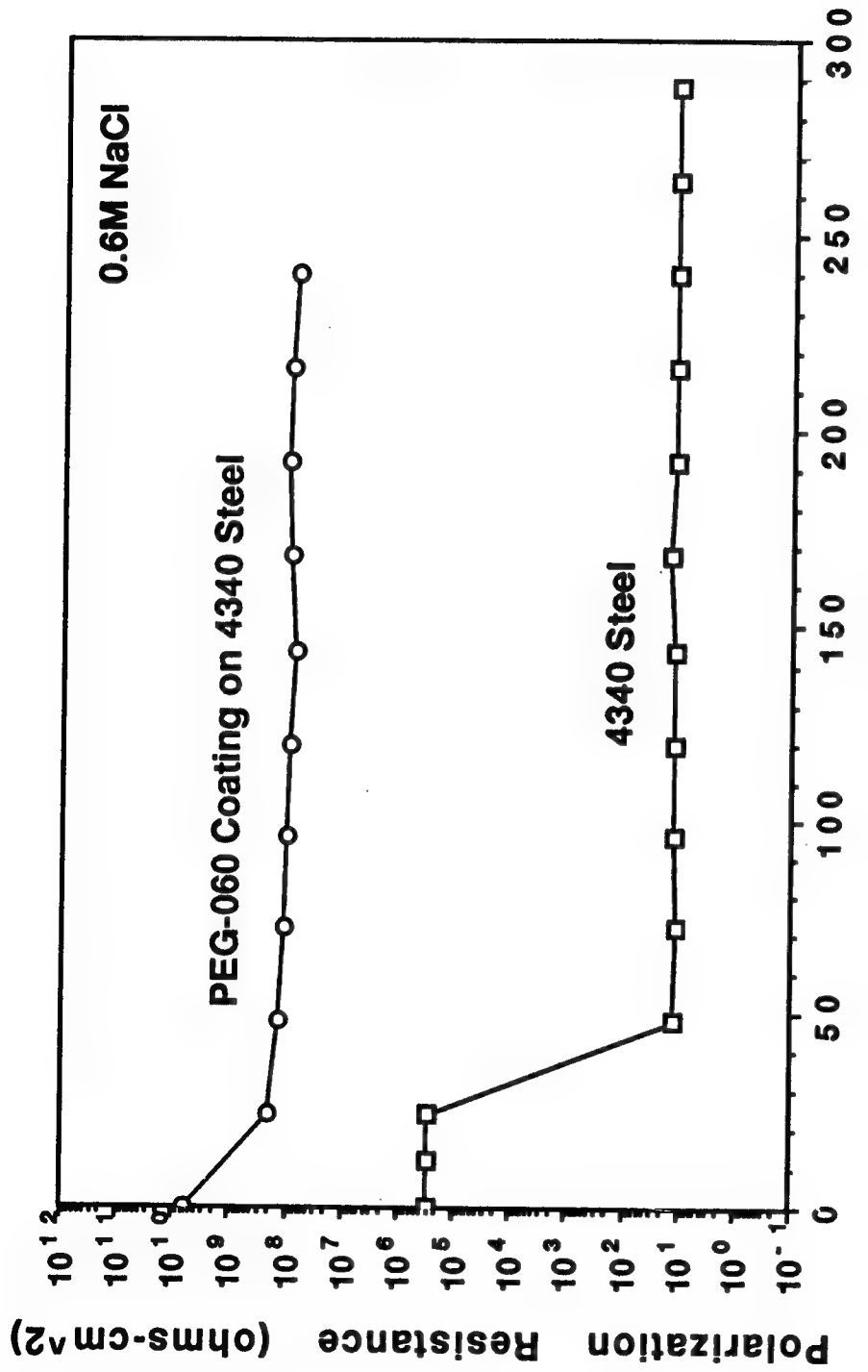

Figure 2. Polarization resistance vs. time for 4340 steel with a PEG-060 coating and untreated 4340 steel.

Exposure to CG-59 Consortia

Samples were made in varying degrees of rigidity by changing the ratio of pre-polymer to cross-linking catalyst. The silicon coated and untreated 4340 samples were then exposed to the CG-59 mixed community of marine microorganisms which contains sulfate-reducing bacteria for 110 days. Environmental Scanning Electron Microscopy (ESEM) examination showed that the untreated 4340 steel coupons had undergone corrosion and that microbial colonization had occurred, see Figure 3. ESEM examination has also shown that, in general, portions of the PEG-015 and PEG-060 silicone coatings were lightly colonized by the bacteria. Figure 4 shows a region of a PEG-060 coating onto which an inorganic material precipitated. The surface of this sample is relatively clean but there were areas with some light colonization. Figure 5 shows a region on another of the PEG-060 coatings that was heavily colonized by the bacteria adjacent to a clear area. Figure 6 shows a region on a third PEG-060 coated sample in which there was a small defect in the coating which did not extend to the substrate. There was no evidence of bacterial colonization or precipitates in this region.

The PEG samples used in these tests were produced using the mold technique and many of the coatings peeled/separated at the interface produced by the process. This peeling allowed solution contact with the 4340 steel. This, in turn, resulted in corrosion. Therefore, a quantitative correlation between the corrosion behavior, the resistance to bacterial colonization, and polymer to catalyst ratio could not be obtained. However, qualitatively, the relatively light bacterial colonization on the PEG surfaces suggests that it is not a favored surface. Also the "puckering" of the PEG coating (Figure 5) suggests that the bacteria that colonize the surface are not adhering to the entire surface uniformly, i.e. there are discrete attachment sites. The bacteria that colonize these surfaces may therefore be easily removed due to a limited number of attachment sites.

Figure 3. ESEM micrograph of untreated 4340 steel exposed to the CG – 59 bacterial consortia.

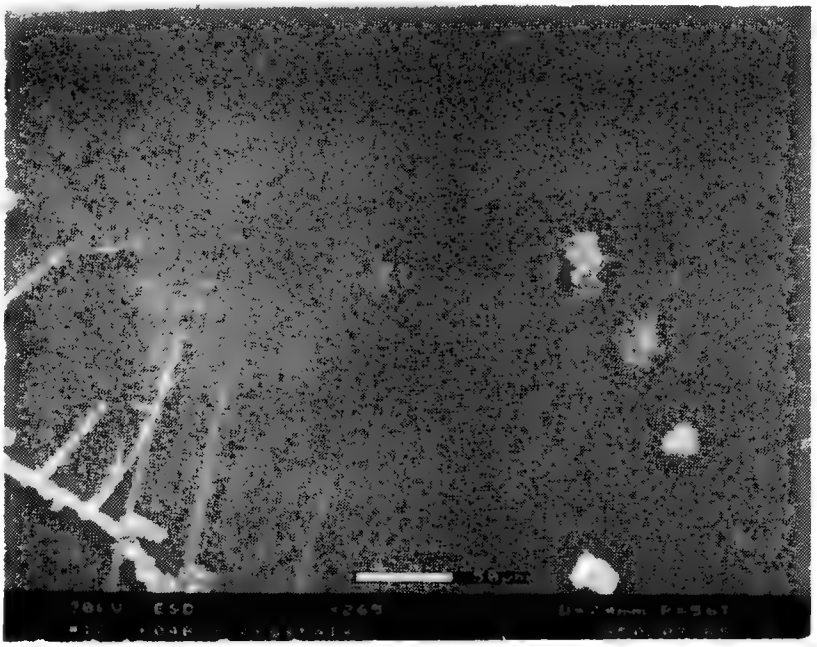

Figure 4. ESEM micrograph of 4340 steel with a PEG – 060 coating exposed to the CG – 59 bacterial consortia.

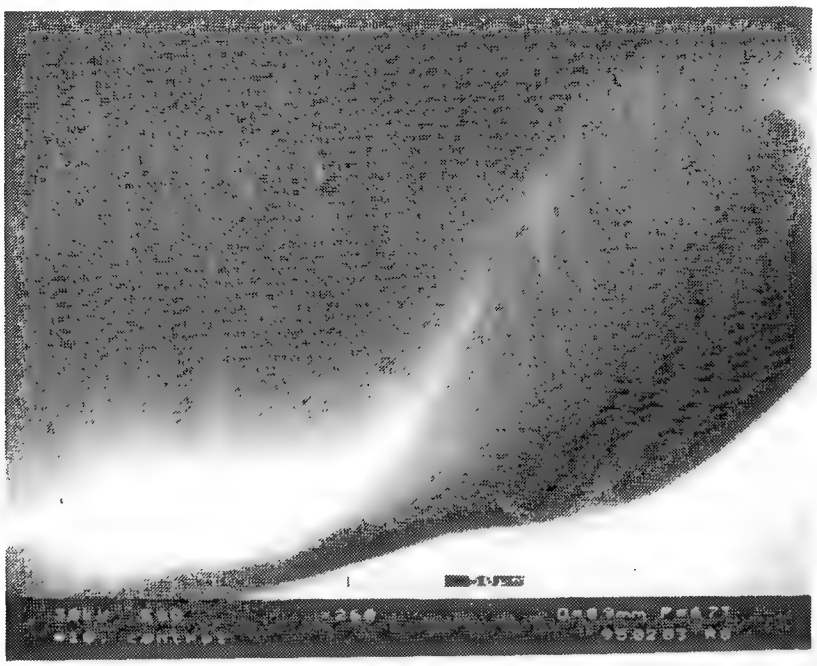

Figure 5. ESEM micrograph of 4340 steel with a PEG – 060 coating exposed to the CG – 59 bacterial consortia.

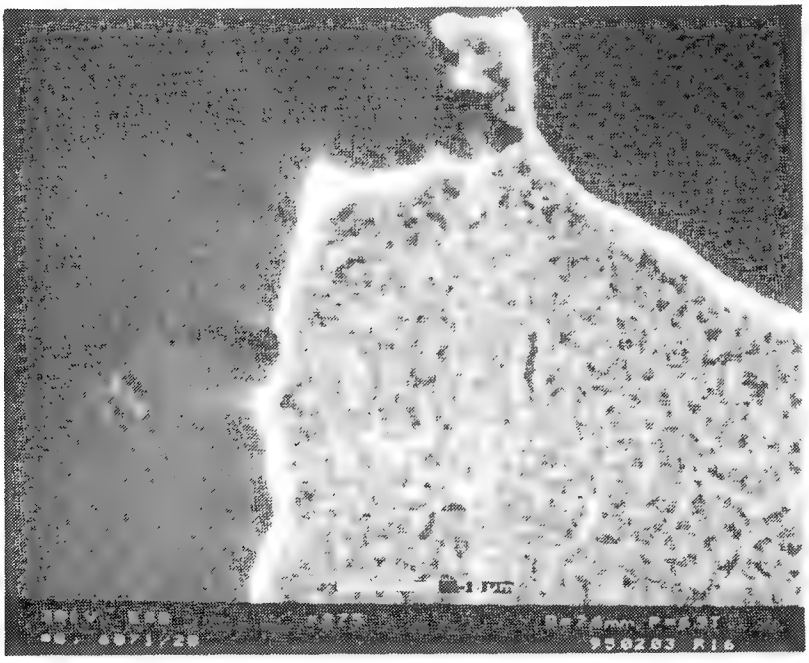

Figure 6. ESEM micrograph of 4340 steel with a PEG – 060 coating exposed to the CG – 59 bacterial consortia.

Exposure to a Marine Environment

Samples were made in 4 degrees of rigidity by use of different ratios of pre-polymer, PEG-015, to cross-linking catalyst. The silicones were then immersed in the estuary at the Smithsonian Laboratory in Edgewater, Maryland for six weeks. The intent of this work was to determine if macroorganisms such as barnacles would attach to the PEG surfaces. No barnacle settlement was observed on the silicone samples but barnacles did settle on the rack used to hold the samples during immersion. There was some algal growth starting at the edge of the samples where the silicone samples were in contact with the sample holder. This growth progressed toward the center of the silicone samples. No samples were completely overgrown and all showed a "clear" area in the central area of the samples. Microscopic observation of the "clear" area showed a sparse population of the remnants of larval tubes of invertebrates such as amphipods, a few nematodes, and swarming organisms similar to paramecia, and a few strands of algal forms traversing the surface. All could be easily dislodged from the surface with a dissecting needle, unlike the barnacles, tubeworms, or bryozoans that were firmly attached on the hard surfaces of the test rack. The most significant finding of this work was that when the samples were arranged in the order of apparent overgrowth, the order was that more growth was observed on the more cross-linked samples, the least growth on the least cross-linked samples, with the exception of one highly cross-linked surface which remained relatively "clean". This ordering would be predicted by a mechanical sensing mechanism of microbial attachment.

The results of the exposure to the CG-59 mixed community of marine microorganisms and to the estuary waters showed that the degree of colonization by organisms was less on the silicone surfaces than on the untreated metal or rigid surfaces. As mentioned above, a property of silicones which may be pertinent in preventing or inhibiting colonization by microorganisms is the high chain mobility of these polymers (20-23). If mobility is very high, there may not be perceptible stresses induced in an attaching organism so that stress-induced

change in the membrane ion flux ratio does not occur. In short, the organisms do not know that they are near a solid surface and therefore do not undergo the metamorphical changes necessary for attachment. Another possibility for the resistance to colonization of these materials is that their interaction with the surface of potential colonizing organism surfaces is weak because no strong bonding can occur. This latter idea is supported by the observations in the medical community that stainless steel heart valves polished with stearic-acid resist "fouling" in the blood stream. Baier (24) has observed that the polishing process coats the metal with a layer of the long-chain fatty acid, so that the surface presented to the medium is a close-packed layer of terminal methyl groups. This surface was suggested to be responsible for the non-fouling nature of the surface because the clean stainless steel became "fouled" within a short time after implantation. Dimethylsilicone chains also presents a surface rich in methyl groups to the environment, so that there is an element of support for this mechanism, especially since the close-packed chains of long-chain fatty acids are not generally considered to be mobile. As other materials bearing methyl-terminated alkyl chains have not proved to be as non-fouling as the dimethyl silicones, it is possible that both factors are involved in the non-fouling phenomenon.

III. Inorganic Inhibitors

A. Background

When a bare metal is exposed to a saltwater environment, it interacts electrochemically with the environment. The interaction can be small as with, for example, metals which develop passive films or it can be large in which case corrosion occurs. In either case, metal ions are introduced into solution via the anodic reaction [1]:

$$M^o \dashrightarrow M^{+z} + z\,e^- \qquad [1]$$

where M^o is a metal atom, M^{+z} is a metal ion, and e^- is an electron. The result is that metal ions are present in the near surface region at concentrations greater than in the bulk aqueous environment. It has been observed that many microorganisms are able to sense and move toward nutrients and other attractants, and move away from harmful substances or other repellents. Movement toward chemical attractants and away from repellents is known as chemotaxis. Microorganisms can respond to very low levels of attractants on the order of 10^{-8} molar, with the magnitude of the response increasing with attractant in this low concentration range (11). Thus it might be expected that metal ions produced by the anodic reaction and which microorganisms need as metabolites could attract microorganisms to the metal surface and/or stimulate or trigger attachment of the microorganism and thereby promote biofilm formation

Gordon et al. (25) have shown that changes in the pH at the metal/seawater interface correlated with attachment of bacteria. The electrochemical and chemical reactions associated with corrosion can effect the local pH. Free metal ions that are produced at the anode can participate in hydrolysis reactions (reaction [2]) thereby lowering the local pH; while oxygen is consumed at the cathode (reaction [3]) resulting in an increase in the local pH.

$$M^{+z} + z\,H_2O \dashrightarrow M(OH)_z + z\,H^+ \quad [2]$$

$$O_2 + 2\,H_2O + 4\,e^- \dashrightarrow 4\,OH^- \quad [3]$$

Therefore, it is possible that the changes in local pH resulting from the electrochemical processes associated with corroding systems can be a stimulus that triggers the adsorption of microorganisms leading to biofilm formation.

If any or all of the electrochemical and/or chemical reactions discussed above provide the stimulus/stimuli that trigger colonization of the metal surface, then an inhibitor that prevents corrosion should also inhibit microbial colonization. A caveat with presently used corrosion inhibitors is that many have been shown to act as nutrients sources for bacteria (4,9) and thereby provide a favorable surface for microorganism colonization. Therefore, another approach to prevent MIC is to use inhibitors that prevent aqueous corrosion but do not act as a major, minor, or trace nutrient sources for microorganisms.

The discussion above considers the metal to play an active role in attracting microorganisms to the surface leading to biofilm formation. The object of this work is to determine if the substrate metal attracts microorganisms through the release of metal ions (corrosion), pH changes (anodic and cathodic processes), or by its surface charge character. To this end, several pure metals were exposed to the CG-59 mixed community of marine microorganisms. To date, the metals exposed are tantalum, tungsten, molybdenum, zirconium, and 4340 steel. The information obtained from the exposure of the pure metals will help to clarify the nature of attraction of microorganisms to metal surfaces and provide a basis for the selection of inorganic compounds that inhibit attachment.

B. Materials and Methods

X-ray photoelectron spectroscopy (XPS) was used to determine the nature of the metal surfaces (tantalum, tungsten, molybdenum, zirconium, and 4340 steel) before immersion. The XPS measurements were made using a monochromatic Al Ka X-ray source. The spot size was 600 μm, the pass energy was 50 eV, and the base pressure was 8 x 10^{-9} torr or lower. The XPS spectra were corrected for charge shifts by normalizing binding energies to that of the adventitious carbon 1s peak at 284.6 eV.

Samples (1/2" square) of tantalum, tungsten, molybdenum, zirconium, and 4340 steel were exposed to the CG-59 bacterial consortium which contains sulfate-reducing bacteria. The tantalum, tungsten, molybdenum, and zirconium were at least 99.99% pure. Tantalum, tungsten, molybdenum, zirconium are also know for their resistance to corrosion. Chromium and niobium were exposed at a latter date and will not be considered in this report.

C. Results and Discussion

Table 2 shows the binding energy values and the predominant surface species present for each of the metals before exposure to the CG-59 marine consortium. These values will be compared with those obtained after exposure.

Table 2. Surface character of the metals before exposure to the CG-59 consortium.

Metal	Binding Energy* (eV)	Predominant Surface Species
4340 steel	710.7	Fe_2O_3, FeOOH
zirconium	178.6	ZrO_2
tantalum	25.8	Ta_2O_5
molybdenum	232.6	MoO_3
tungsten	35.6	WO_3

* Binding energy values normalized to C 1s at 284.6 eV.

Table 3 shows weight changes and calculated corrosion rates for 4340 steel and the pure metals after 120 days of exposure to the CG-59 consortia. These results show that in general the corrosion rates after 120 days are low. The steel is undergoing corrosion in both the control and the CG-59 with the rate of corrosion being slightly higher in the control (Postgates medium plus lactate) environment. The measured differences in the weight before and after exposure to the CG-59 consortia for the tantalum, tungsten, and zirconium samples are essentially non-existent. The molybdenum shows a small but significant weight loss after exposure to the CG-59 consortium. Visual examination of the samples showed the tantalum, tungsten, molybdenum, and zirconium were shinny with no visible sign of corrosion; in contrast, the 4340 steel had darkened and pits could seen on the surface.

Table 2. The weight loss and corrosion rates for 4340 steel and the pure metals after 120 days exposure exposed to CG-59.

Material	Control		CG-59	
	weight loss grams ($x10^{-4}$)	MPY ($x10^{-5}$)	weight loss grams ($x\ 10^{-4}$)	MPY ($x10^{-5}$)
4340 steel	168	160	137	130
zirconium	0	0	1	1
tungsten	50	19	0	0
tantalum	7	3.1	8	3.6
molybdenum	18	13	101	74

Of the metals chosen tantalum, tungsten, and zirconium do not play a role in the life cycle of microorganisms; molybdenum is used as a trace nutrient, and iron (from 4340 steel) is a major nutrient (26). These initial results indicate that a relationship between corrosion, the nutrient quality of the substrate, and MIC may exist.

IV. Summary

Two candidate polydimethylsiloxane polymers, PEG-015 and PEG-060, were selected based on the mechanical sensing mechanism of microbial attachment. The steel coated with these materials had essentially non-existent corrosion rates, the extremely stable anodic and cathodic polarization behavior, and high polarization resistance values determined using *ac* impedance. These results show that the silicone compounds produce an effective barrier to abiotic corrosion in 0.6M NaCl solutions. Also, using the dip technique coatings were produced in thicknesses of engineering significance. The results of exposure of the PEG compounds to the CG-59 mixed community of marine microorganisms and to the estuary waters showed that the degree of colonization by organism was less on the silicone surfaces than on the untreated metal or rigid surfaces. The relatively light colonization on the PEG surfaces suggests that is not a favored surface.

Preliminary results from the exposure of tantalum, tungsten, zirconium, molybdenum, and 4340 steel to the CG-59 consortium show that in general the corrosion rates after 120 days are low. The steel has undergone corrosion in both the control and the CG-59 with the rate of corrosion being slightly higher in the control environment. The measured differences in the weight before and after exposure for the tantalum, tungsten, and zirconium samples are essentially non-existent; while the molybdenum shows a small but significant weight loss after exposure to the CG-59 consortium. Tantalum, tungsten, and zirconium do not play a role the microorganism life cycle; molybdenum is used as trace nutrient, and iron (from 4340 steel) is a major nutrient. These initial results indicate that a relationship between corrosion, the nutrient quality of the substrate, and MIC may exist.

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